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SORPTION PHENOMENA OF NICOTINE AND ETHENYLPYRIDINE VAPOURS ON DIFFERENT MATERIALS IN A TEST CHAMBER

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ABSTRACT

The sorption phenomena that nicotine undergoes in indoor environments have long been recognized as a severe limitation in its use as a marker for environmental tobacco smoke (ETS). This paper proposes an empirical description of these phenomena, and compares them to those undergone by another potential marker, ethenylpyridine, under the same conditions. The sorption of both compounds onto different surfaces (glass panes, cotton, wool, and nylon fabrics) has been investigated through dynamic experiments carried out in a 1-m³ glass chamber. Their kinetics were determined both under initial conditions of equilibrium between gas and adsorbed phases, and out of equilibrium. The combined influence of relative humidity and of the nature of the sink system on the sorption of each compound is outlined. These results can be used to predict the dynamics and magnitude of these processes, and the significant biases that they are likely to cause when nicotine is used to assess low-level ETS exposures are addressed. Milligram amounts of nicotine could be adsorbed and re-emitted from 1 m² of cotton cloth over a few hours. Biases may be caused by the re-emission of adsorbed nicotine after ETS has been essentially cleared by air exchange, or by transport on clothing and subsequent re-emission. The relative importance of these biases increases as aging ETS is increasingly diluted through ventilation.

INTRODUCTION

In indoor air quality surveys, nicotine, the major tobacco alkaloid, is the most widely used chemical marker in the assessment of exposure to ETS. This is because, though it is not unique to tobacco, its presence in indoor air is generally assumed to be the specific result of the combustion of tobacco. Despite its low volatility, nicotine is almost totally found in the gas-phase of ETS, and can therefore rapidly diffuse to surfaces with which it may interact. The strength of the resulting sorption effects has been given as a reason for the poor correlation that is often observed between nicotine levels and the concentrations of other ETS constituents (1), but, possibly for lack of quantitative data, these effects are seldom taken into account in discussions or calculations. Some authors have advocated using ethenylpyridine (EP), a pyrolytic decomposition product of nicotine, as a marker because not only is it as specific, but it also does not appear to be affected by sorption effects to the same extent as nicotine (2). The present study aimed at proposing an empirical model for the nicotine sorption dynamics, and at assessing quantitatively their importance. To assess the impact of these effects on the validity of the use of nicotine as a marker, EP sorption was also compared to that of nicotine by performing many experiments on both compounds simultaneously.

METHODS

The sorption of both test compounds, nicotine and EP, was evaluated in a 1-m³ glass chamber designed in accordance with the recommendations published in (3). The chamber was supplied with clean air at a constant relative humidity, so as to maintain a preset air-exchange rate. Experiments were carried out with the empty chamber or in the presence of certain materials enclosed in it, the experimental conditions being chosen so that the results could be applicable to normal levels of ambient nicotine in indoor environments. A large set of experiments was performed close to equilibrium, with an adsorption phase during which either nicotine alone or both compounds were fed into the initially clean chamber at a constant rate, followed by a desorption phase during which the chamber was purged with clean air. A modeling of nicotine and EP sorption processes was then deduced from their concentration in the chamber as a function of time. The second set of experiments addressed conditions that were far from equilibrium. It included, for both compounds, the uptake by a sample exposed to a constant air

concentration and the release into clean air from a pre-loaded test material. The kinetics of the return to equilibrium were followed. Since the scope of the study was to assess the sorption phenomena on a time scale of at most a day, any sorption phase was limited to a maximum duration of three days.

Most of the EP tests were performed using the 4-isomer, which is commercially available (Sigma). Some experiments were carried out using synthetic 3-ethenylpyridine, the isomer found in ETS. This ensured that the isomer substitution had no sizable influence on the results. Nicotine and EP air concentrations were monitored simultaneously according to (4). In most studies, additional small pieces of the material under investigation (or glass pieces) were placed into the chamber. After being exposed in the chamber for defined periods of time, they were removed for analysis. The samples were immediately extracted and analyzed as above (4).

Nicotine and EP were introduced into the chamber by use of heated all-glass diffusers. The rates of introduction being critical parameters in the experiments, a calibration of the diffusers' output was performed by trapping the emitted substances in a series of annular denuders with a citric acid coating. An independent check on these rates was also provided by the analysis of the sink material (see match of mass balance with analytical results, Figure 2).

Wool, cotton, and nylon are the predominant materials in clothing or indoor coverings. Cotton and wool are rather hydrophilic, as shown by their water regain, whereas nylon is much less so. Cotton and nylon were thus selected for the study as two different, yet commonly encountered materials, and in intake and release experiments a wool-based clothing material was also tested. The samples, purchased on the open market in Switzerland, were machine-washed before being used. Detailed information about the origin or preparation of the samples was not available, but the cotton and nylon materials appeared white, indicating minimal or no dyeing. Two faces of the chamber were covered with the material to be evaluated. This loading factor (2 m^{-1}) was expected to keep the relative influence of the glass surfaces minimal. To estimate this influence, some experiments were performed with the chamber empty (i.e. glass sink system).

The statistical curve fittings were carried out using the NLIN non-linear regression routines of the SAS[®] package. The performance of 3 optimization methods, namely DUD, Gauss, and Gauss-Newton was compared when applied to the simpler models. More convergence problems were experienced with the Gauss-Newton method, while the DUD method was in our case the best. One additional advantage of the DUD algorithm was that explicit expressions of the first and second derivatives of the response function are not needed. DUD was thus applied to all other models.

RESULTS

Data treatment

Figure 1 shows the profile of nicotine concentration (adsorption and desorption phases) with 2 m^2 of cotton in the chamber. The curves which would have been observed in the absence of any sorption and assuming a perfect mixing (exponentials from the dilution model) have been added. The amounts of nicotine found in the sink material during the adsorption phase are plotted in Figure 2. Figure 3 shows the same profiles, but at constant air concentration (intake). Selecting a suitable kinetic scheme to represent the sink dynamics was a prerequisite to the assessment of the processes. A first consideration was that what appeared to be a steady state concentration was indeed reached at the end of the adsorption phase, but, at least in the nicotine results, it was always significantly lower than expected. A thorough verification of the accuracy of the introduction rates of the compounds ensured that a systematic error in the diffuser calibrations was not the cause for this observation. This phenomenon could be rationalized by the occurrence, during the adsorption phase, of a removal process with a constant rate at the steady state (within the experiments time frame). It could thus be treated as an "irreversible" removal. Such a sink has been described by several authors, who accounted for it by incorporating a first order removal into the kinetic scheme (5, 6), the first order rate being essentially chosen for the relative simplicity of the equations (it simply adds to the air-exchange rate of the chamber).

After the contribution of a suitable "irreversible" removal was taken into account, the measured data were, in all experiments, still lower than expected in the early part of the adsorption phase, and higher in the early part of the desorption phase. This could be taken into account by adding

to the scheme a reversible sink (loaded until it is saturated, and subsequently unloaded into the system in the desorption phase). A mathematical model for this combination of sinks has been given by Dunn (6) and these equations were used to perform the non-linear fitting of the data. The results are summarized in Table 1. A simple resolution of the kinetic parameters was performed in parallel to test the practicality of such an approach. Quantifying the "irreversible" process from the steady state concentration was straightforward, and the mass taken up at equilibrium by the reversible sink could simply be estimated from the concentration curves without any assumptions regarding the kinetics of the phenomenon. This mass is proportional to the

Figure 1: Nicotine concentration profile in chamber (cotton sink)

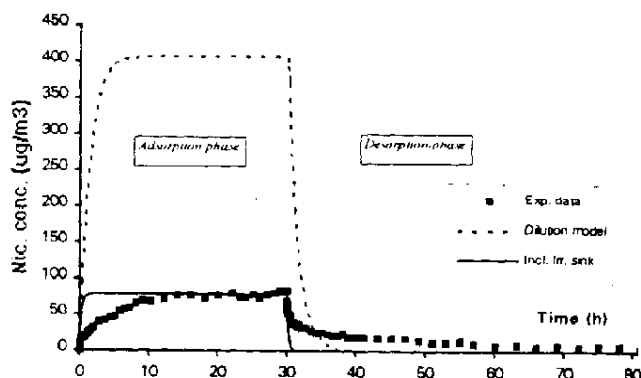
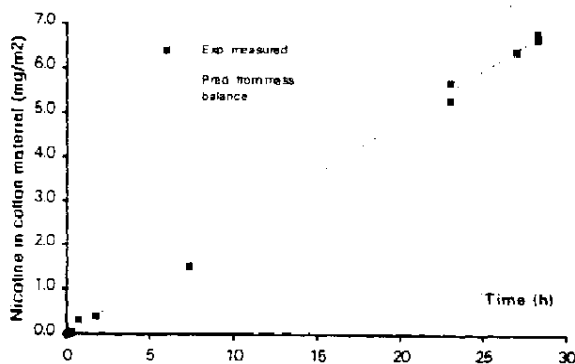


Figure 2: Nicotine found and predicted from mass balance



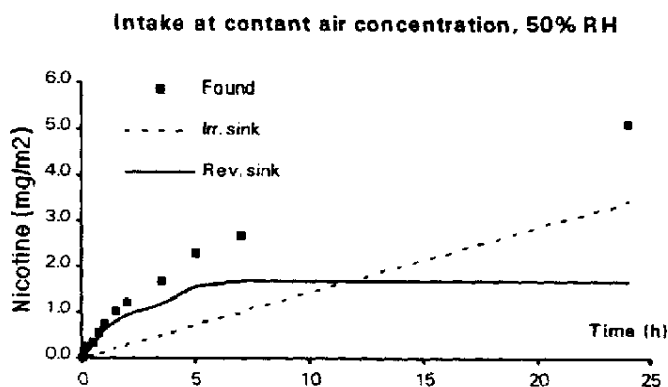
area between the experimental concentration curve and the one that would be expected in the absence of the reversible sink, and can thus be computed using trapezoid constructions (3). It could be hypothesized that the "irreversible" sink would be a deeper and more strongly bound state for molecules that would first have been reversibly adsorbed into a superficial sink. In this alternate scheme, the two sinks would be linked in series. To test this hypothesis, a model was constructed with two additional constants reflecting the transfers between a first and a second

reversible sink. Such a two-compartment model for the reversible sink was, for instance, described by Guo (7). The "irreversible" sink was kept in the new model to determine its contribution, if any. The corresponding set of differential equations was resolved mathematically, and the equations for the solution fitted to the experimental data. Compared to the model with a single reversible sink, fitting the data using the two-compartment model led to an unchanged contribution from the irreversible sink and no meaningful impact from the deeper stage of the reversible sinks, meaning that both

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Figure 3: Nicotine in cotton, contribution from each sink



sinks should indeed be considered as operating in parallel, independently from each other.

The results of the direct computations were identical to those of the non-linear fittings, although they were more sensitive to the experimental noise. Those derived from the adsorption phase data were in agreement with those from desorption phase data, but their computation was more reliable.

Discussion

Correction for the chamber walls.

An attempt was made to determine the influence of chamber walls and correct for it. The rate of the "irreversible" sorption to different parts of the system is simply the sum of each contribution. The influence of relative humidity and compound level on these rates could be empirically derived for nicotine in a glass system and this contribution was subtracted in the other experiments. It was always smaller than the cloth contribution, and hardly measurable for EP. These models were used to derive predictions for the comparison with results of intake experiments. For the reversible sink, the glass contribution appeared relatively small compared to that of cotton, and a crude calculation assuming additivity was made. The wall effects were overwhelming in the nylon experiments.

Influence of experimental conditions.

The influence of relative humidity on the sorption processes was quite substantial (Table 2). A change from 40 to 70% resulted in the sorption parameters varying by a factor of 2 to 3 in most instances. Surface-adsorbed water can impact the process in opposite ways, through competition for active sites (a) or by dissolution into the water film of highly water-soluble compounds like nicotine (b). Process (a) had the largest impact for EP whereas (b) appeared predominant for nicotine reversible sorption to glass, wool and nylon.

Dynamics out of equilibrium ("Intake" and "Release" experiments).

The kinetic model appeared to remain valid in intake or release experiments. The only fitting that could be done on these data was to split the nicotine amounts in the cloth (intake experiments) into a linear part (loading of the irreversible sink) and the remainder attributable to the reversible sink (Figure 3). The results are listed in Table 3. The irreversible loading rates are in good agreement with the values predicted from the equilibrium experiment results. The reversibly adsorbed mass seemed to be increased in uptake experiments, but this could be due to the fact that the reverse side of the samples was somewhat exposed as well. The time for the full loading of the fast reversible sink was reduced to about 5 hours. The amounts released in the release experiments seemed consistent with the loadings from both reversible and irreversible sinks. This implies that a release from the "irreversible" sink is likely to be taking place, superposed to that from the faster reversible sink. Because of the experimental noise, no inflection could be observed that could be used to separate both effects. Despite a disproportionate loading in EP, its presence in the chamber air was not measurable after 3 days whereas nicotine level was still half of the peak value.

CONCLUSION

The sorption processes undergone by nicotine and EP with different sink systems were quantified for gas-phase concentrations in the 20 to 300 $\mu\text{g}/\text{m}^3$ range. Differences in relative humidity or sink surfaces resulted in rather large variations in the magnitude and rate of these

Figure 4: Release from a loaded cotton cloth

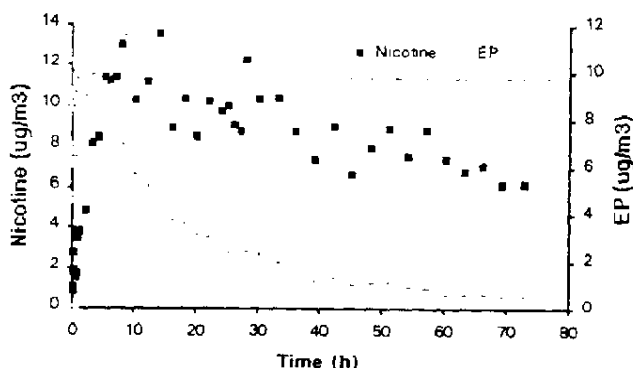


Table 1: Steady state values for air concentration (C equ), mass loading rate into "irreversible" sink, and mass at equilibrium in reversible sink for total system and per m² of material (estimated, see text).

Exp. conditions		Nicotine				Ethenylpyridine			
Material (ACH)	R.H. (%)	C equil. (μg/m ³)	I. uptake μg/m ² h	Rev ads tot (μg)	Rev ads (μg/m ²)	C equil. (μg/m ³)	I. uptake μg/m ² h	Rev ads tot (μg)	Rev ads (μg/m ²)
Glass (1.0)	41	98	6.2	150	25	153	0.41	n.d.	n.d.
Glass (0.98)	60	86	11.8	150	25	0	-	-	-
Glass (1.0)	72	69	13.2	160	27	153	0.33	140	23
Glass (0.95)	53	120	7.0	405	68	136	<0.1	115	19
Glass (0.49)	60	195	10.1	345	57	357	2.5	260	43
Glass (1.44)	60	23	6.3	40	6.7	0	-	-	-
Glass (0.73)	69	123	15.4	310	52	157	n.d.	180	30
Cotton (1.0)	38	26	51	715	~345	116	9.0	210	~80
Cotton (1.11)	72	24	33	225	~100	126	<1	210	~65
Cotton (0.84)	40	212	240	8400	~4100*	160	7.7	350	~135
Cotton (0.72)	32	330	466	15100	~7400*	280	10	715	~290
Cotton (0.70)	69	82	96	1600	~730	185	5.6	195	~50
Cotton (1.0)	64	27	54	n.d.	n.d.	0	-	-	-
Cotton (1.0)	53	25	52	n.d.	n.d.	0	-	-	-
Cotton (0.55)	50	28	51	n.d.	n.d.	0	-	-	-
Nylon (1.13)	76	40	16	440	~190	141	<1	80	<10
Nylon (1.0)	41	80	18	225	~90	160	4.0	25	<10
Nylon (0.98)	62	132	19	700	~270	0	-	-	-
Nylon (0.49)	62	71	19	n.d.	n.d.	0	-	-	-

* Steady state not quite achieved: underestimation of sink capacity and discrepant values from adsorption versus desorption data sets.

Table 2: Estimated uptake rate into "irreversible" sink and equilibrium constant to the reversible sink k_e at 40 and 70 % RH. Computed for concentrations of 100 μg/m³ (nicotine) and 150 μg/m³ (EP).

Material	Nicotine				Ethenylpyridine			
	40 % Irr. rate (h ⁻¹)	70 % Irr. rate (h ⁻¹)	k_e at 40 % RH	k_e at 70 % RH	40 % Irr. rate (h ⁻¹)	70 % Irr. rate (h ⁻¹)	k_e at 40 % RH	k_e at 70 % RH
Glass	0.05	0.14	0.3	0.4	0.003	< 0.002	n.d.	0.15
Cotton	1.54	1.16	18-22	4-9	0.03	0.01	1.1	0.7
Nylon	0.19	0.19	2	5	0.02	< 0.001	< glass	< glass

Table 3: Uptake rate to "irreversible" sink and reversible-sink adsorbed masses in constant nicotine-level experiments compared with predictions from equilibrium experiments.

Material (ACH)	R.H. (%)	Nicotine concentration (μg/m ³)	Irreversible uptake rate (h ⁻¹)		Reversibly adsorbed mass (μg/m ²)	
			found	predicted	found	predicted
Cotton (0.8)	40	80	1.3	1.6	1960	1550
Cotton (1.0)	50	94	1.4	1.5	1690	-
Cotton (0.7)	59	300	0.6	0.9	5440	-
Wool (0.7)	32	70	0.07	-	400	-
Wool (1.1)	50	95	0.16	-	710	-
Wool (0.8)	69	75	0.36	-	780	-

processes, a striking demonstration of the complexity of this type of research. A simple scheme comprising two sinks with quite different kinetics was found, however, to provide a rather satisfactory model. The first sink was characterized by the fact that it reached equilibrium within a few hours. The second sink was found not to stem from the first one, but to occur in parallel to it. Its time constant was much longer, so that, within the time-frame of this study, it could be considered as an "irreversible" process in the experiments close to equilibrium. A very slow release from it could be detected in desorption experiments of loaded materials into clean air.

A rapid and direct approach to characterize the kinetic parameters of a test system was found to be comparable to the more rigorous and complex approach of solving the differential equations describing the scheme and effecting a non-linear fitting on the data. All determinations were made difficult by the fact that they were performed at low gas-phase concentrations.

When comparing the sorption of nicotine to that of EP, the most notable difference was found in the "irreversible" process, quite significant for nicotine and hardly measurable for EP. The strength of the fast, reversible sink, was also substantially greater for nicotine than for EP, the ratios between both equilibrium constants being 3 to 5 for glass or cotton sinks. The difference in vapor pressure between the two compounds was clearly one reason for these discrepancies. These compounds also have rather different water-solubilities, and this could account in part for the much larger sorption undergone by nicotine and the different impact of air humidity. The re-emission from the fast reversible sink could lead to systematic errors when nicotine concentration is used as a marker for ETS exposures. Up to milligrams per m² are involved for nicotine onto cotton (much less for EP) which, though moderate in an absolute sense, is sufficiently large to warrant serious concerns when dealing with very low (or non-existent) ETS levels. Scenarios in which a bias could happen fall into two types. Nicotine could be re-emitted from surfaces after the smoke would have been essentially cleared. This would notably result in over-estimations of the exposures when monitoring through discrete samplings in situations of intermittent smoking. Nicotine could also be re-emitted from mobile surfaces such as clothing after transport into ETS-free areas. Both scenarios would be a cause of systematic errors in the assessment of the general population exposure, and the latter one could result in false alarms when checking that no leaks occur from separated smoking areas.

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